



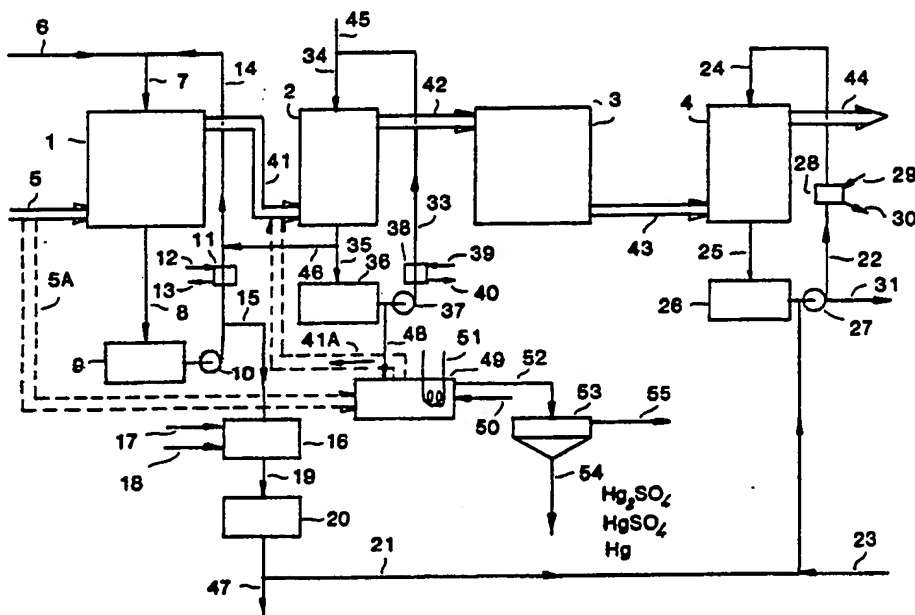
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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**(54) Title:** A METHOD FOR PRODUCING PURE SULPHURIC ACID AND A HIGH-GRADE MERCURY PRO-  
DUCT FROM GASES THAT CONTAIN SULPHUR DIOXIDE AND MERCURY

**(57) Abstract**

Method in the production of sulphuric acid from sulphur-di-oxide containing gas obtained when treating mercury-containing raw materials and intermediate products, for obtaining pure sulphuric acid and a high-grade mercury product. The gas is cleansed from accompanying gaseous mercury, by contacting the gas with sulphuric-acid solution in one or more stages (1, 2), so that the major part of the mercury is absorbed and dissolved in a concentrated solution having a sulphuric-acid concentration of at least about 85%, whereafter the purified gas is passed through a contact plant (3, 4) for producing purified sulphuric acid. The method is characterised by removing a part quantity (48) of the concentrated sulphuric-acid solution (33), and diluting the part quantity to a sulphuric-acid concentration of about 80%, or there below, the major part of the mercury dissolved in the sulphuric-acid solution being separated therefrom in the form of a high-grade mercury product (54) which, if so desired, can be separated from the solution (52). The sulphuric-acid solution can then be purified of residual, dissolved mercury, whereafter the sulphuric-acid solution, free of mercury, can be removed for use in its present form, or can be passed to an absorption tower (4) in the contact plant, for the production of pure, concentrated sulphuric-acid.



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A METHOD FOR PRODUCING PURE SULPHURIC ACID AND A  
HIGH-GRADE MERCURY PRODUCT FROM GASES THAT CONTAIN  
SULPHUR DIOXIDE AND MERCURY

- 5 The present invention relates to a method for producing pure sulphuric acid and a high-grade mercury product in the manufacture of sulphuric acid from a gas which contains sulphur dioxide and which is obtained when treating mercury-containing raw materials and intermediate products, the gas being cleansed of gaseous mercury
- 10 accompanying said gas, by contacting the gas with a sulphuric-acid solution in one or more stages, so that the major part of the mercury is taken-up by and dissolved in a concentrated solution with a sulphuric-acid concentration of at least about 85%.
- 15 By mercury-containing raw materials is meant primarily metal sulphides, such as pyrite, chalcopyrite, zinc-blende and cinnabar, while by intermediate products is meant primarily mercury-containing sludge, deriving, for example, from wet-gas and dry-gas cleansing processes. The sulphur-dioxide-containing gases referred to are primarily roaster
- 20 gases obtained when roasting sulphidic minerals, although gases obtained when working-up intermediate products that contain mercury, may also form part of the sulphur-dioxide-containing gas.
- More and more attention is now being paid to the presence of mercury in industrial processes, and the risks associated therewith.
- 25 As will be understood, the problems involved become more significant when the products concerned are fertilisers and foodstuffs. Extremely large quantities of sulphuric acid are used in the manufacture of these products, and consequently, the sulphuric acid should contain
- 30 as little mercury as possible. Mercury is also liable to be introduced into process or product chains through other processes which have no direct connection with said product, giving rise to obvious risks of contamination.
- 35 Sulphuric acid which is contaminated with mercury can also be obtained from sulphuric-acid manufacturing plants based on the roasting of metal sulphides, for example, pyrite, or zinc-blende,

when the roaster gases are not cleansed thoroughly enough. Even though the gas is cleansed adequately, breakdowns in the operation of such sulphuric-acid plants can, at times, result in gases which are highly contaminated with mercury.

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The roaster gases generated when roasting sulphide materials are passed from the roaster to, for example, a cyclone, where the gases are cleansed from coarse dust particles accompanying said gases. The gases are then cooled and dry-cleansed in, for example, a Cottrell precipitator. Final cleansing of the gas is effected, for example, by washing the gas in washing towers with subsequent wet-Cottrell filters. There is normally no difficulty in expelling mercury compounds, and consequently the major part of the mercury present in the material will be incorporated in the roaster gas in the form of mercury compounds and elementary mercury in particle or vapour form. Substantially all the mercury compounds present in the gas can be separated therefrom in particle form, by means of such gas-cleansing systems. Despite this, however, it is impossible to control the roasting and gas-cleansing processes in a manner to ensure that the amount of elementary gaseous mercury contained in the dust-freed gas is sufficiently low to enable the gas to be used in other processes, or to be discharged to a recipient. Consequently, mercury vapour accompanies the gas through the whole of the sulphuric-acid process, and is finally absorbed in the end product, i.e. the sulphuric acid. This contaminates the acid and also represents a loss of valuable mercury.

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In an attempt to alleviate these problems, various purifying processes have been proposed, in accordance with which, either the sulphuric acid is treated in a manner to precipitate its mercury content, or the roaster gas is washed, or treated in some other way, to eliminate its mercury content, prior to passing the gas through the sulphuric-acid plant. The choice between these two alternatives, i.e. sulphuric-acid purification or roaster-gas washing is primarily decided by local conditions, for example, by whether or not the existing

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relevant plants are available, whether or not the equipment available is good enough to effect a wet-gas cleansing process satisfactorily, or whether or not the space available is sufficient to carry out the cleansing process. The alternative selected is also determined by the level of the mercury present and the variations in said level. In many cases it has been found that those methods, which include the purification of the sulphuric acid are to be preferred.

A purifying method for this purpose requires firstly that low residual contents of mercury can be achieved in the sulphuric acid and secondly that the precipitated mercury-containing material can be removed from the acid. When carrying out such purifying processes, it is not permitted for other toxic substances, such as lead and arsenic, to be introduced into the acid. In certain cases, fast acting processes are required, for example so as to limit the corrosion attack on apparatus contained in the purifying plant when handling dilute acids and washing liquors.

The German Patent Specification No. DE-C-I 216263 describes a method in which concentrated sulphuric acid is treated with relatively coarse particulate elementary sulphur. The residual contents obtained, however, are not acceptable in view of the fact that many countries have stringent requirements with respect to the deposition of heavy metals.

Mercury can also be precipitated from sulphuric acid, diluted or concentrated, by treating the acid with sulphides or hydrogen sulphides. The disadvantages with these methods, described for example in the German Patent Specifications, DE-C-I 054972 and I 124024, are that the acid can be contaminated by metals introduced as metal sulphides, and that it is difficult to separate the precipitated mercury compounds from the acid. Account must also be taken of the hygiene risks created when producing or using hydrogen sulphide.

Mercury is precipitated from the sulphuric acid very rapidly when, in accordance with SE-B-369295, elementary finely-divided sulphur is precipitated in the sulphuric acid, by adding thereto a sulphur compound, which decomposes in the acid to form colloidal sulphur, on which mercury present in the acid is adsorbed. The sulphur compound may comprise  $H_2S$  or  $Na_2S$ , although thiosulphate is preferred. Subsequent to separating the solid mercury-containing substance by filtration, the residual mercury-content of the acid is extremely low. This separation, however, is encumbered with some difficulties, due to the large specific surface area of the sulphur. In addition, since large volumes of acid must be treated, the filtering process is extremely time consuming. Although other separation methods have been proposed, none of these has been able to compete with the filtering method, despite the problems associated with such methods.

Methods have also been proposed in which the tendency of the sulphuric acid to dissolve mercury, at least at high acid concentrations, is utilised for cleansing roaster gases. One such method, in which the gas is cleansed in a single stage at elevated temperature with a sulphuric acid concentration of 85-90% is described, for example in DE-B-2 132231.

Another method, in which the gas can be cleansed in several stages, is described in DE-B-2 243 577. According to this method, mercury is first removed from moist roaster gas, by washing the gas with sulphuric-acid washing solutions in conjunction with drying the gas and then precipitated from the sulphuric-acid solutions, in sulphide or selenide form, in certain cases in conjunction with the reduction of certain metals. The washing acids used have concentrations of between 30 and 99%. Mercury is not absorbed to any noticeable extent, until an acid concentration of about 70%  $H_2SO_4$  is reached. The sulphuric-acid purification process combined with the washing system is also encumbered with the afore-described disadvantages, concerning the introduction of other impurities into the acid. Difficult problems in separating the mercury from the acid are also experienced.

The treatment of roaster gases in two (or more) stages at different acid concentrations, as employed in the previous method, is also described in DE-B-1 792 573 in conjunction with a method for avoiding the manufacture of 'black' acid from roaster gases that contain organic compounds.

A further development of the aforementioned processes which utilise sulphuric acid as a medium for eliminating mercury vapour from roaster gases is described in our earlier Patent Specification SE-B 7307048-4, in accordance with which concentrated sulphuric acid which contains mercury is also supplied and utilised for mercury-absorption in the first stage, and then purified. As previously indicated, since when carrying out the method all mercury supplied to the process, both through the gas and through contaminated sulphuric acid, shall be removed by treating acids from the first process circuit in a manner to precipitate the mercury contained in said acids, the previously mentioned separation problems will occur, unless the sulphuric-acid purifying stages are dimensioned with respect hereto. Because of this, the investment costs and operation costs are often prohibitive, at least when large quantities of mercury are to be charged to the system.

Thus, none of the purifying methods mentioned above fulfills the requirements mentioned in the introduction with respect to low residual contents of mercury and other metals in the sulphuric acid produced, and that it must be possible to isolate effectively the mercury compounds removed. As beforementioned, the best methods from the aspect of purifying sulphuric acid, namely those methods based on forming a finely-divided sulphur-phase in the sulphuric acid in order to adsorb the mercury, are encumbered with difficult separation problems. In addition, this means that the possibility of treating materials which are more rich in mercury than others is restricted, since wide variations in the ingoing mercury content cannot be tolerated unless the purifying apparatus has been initially over-dimensioned. Furthermore, all of the mercury product recovered

will be of a low grade, since during the purifying process other impurities in the acid, among others, selenium, which is often present in the acid, will also be adsorbed at the same time on the precipitated sulphur-phase, thereby to contaminate the sulphur itself and the added filter aid and to substantially 'dilute' the separated mercury product. At present, there are to be found large quantities of such low-grade mercury-containing products, obtained, inter alia, from gas-cleansing filters and washing apparatus, which cannot be worked-up economically, and which merely constitutes a dumping problem and consequently also a potential threat to the environment.

Surprisingly, it has now been found possible to provide a method by which the aforementioned problems encountered when using mercury-containing gases that also contain sulphur-dioxide for producing sulphuric acid are substantially eliminated. The method also enables the major part of the gaseous mercury in the gas to be recovered, in the form of a high-grade mercury product, which can be worked-up into useful mercury products, without requiring large investments to be made. The method can also be applied advantageously for working-up or refining mercury-containing intermediate products into high-grade products, for example, such intermediate products as those obtained when separating particulate mercury compounds from mercury-contaminated gases in gas-cleansing systems.

As mentioned in the introduction, the present invention is based on absorbing mercury in sulphuric acid of high concentration in one or more stages, and is characterised by the steps set forth in the accompanying claims. Thus, the method involves absorbing the major part of the elementary mercury accompanying the gas in sulphuric acid having a concentration of at least 85%, from which mercury is recovered by diluting the concentrated acid to a given level at which mercury-ions present in the acid have a low solubility. In this way, there is quickly obtained a high-grade mercury precipitate which can readily be separated from the acid and which can readily



be worked-up into a commercially valuable product, such as metallic mercury for example. This also greatly facilitates any final purification to which the acid might be subjected, since the major part of the mercury has been removed from the acid in earlier stages.

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The invention will now be described in more detail with reference to the accompanying drawings and Examples, of which drawings Figure 1 is a diagram illustrating the dilution requirement, Figure 2 is a block schematic of a preferred embodiment of the invention, and  
10 Figures 3 and 4 are diagrams illustrating the purification effect obtained with different acid concentrations and acid temperatures respectively.

Thus, in accordance with the invention, the acid is diluted so as to  
15 obtain a concentration less than at least 80%. Even though in certain cases concentrations below 50% may be desirable, it is naturally preferred to dilute as little as possible, and the optimal range is thus from 50-75%.

20 When the acid is diluted to concentrations beneath 60-65% (somewhat varying, due to temperature), the amount of mercury precipitated is not correspondingly as large, but instead some mercury is re-dissolved. It has been found, however, that this tendency of the mercury to re-dissolve is counteracted when sulphur dioxide  
25 is added while diluting the acid and that further dilution of the acid in the presence of  $\text{SO}_2$ , results in a further lowering of the mercury content to as little as  $< 1 \text{ g/t}$ . In certain cases it may be desirable to utilise this fact in order to reduce the mercury content of the part flow in a single purifying stage to such a low  
30 level as to enable the part flow to be fed to the absorption circuit without contaminating the product acid to any appreciable extent, or without diluting said acid to an extent which would disturb the water balance.

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This may even be preferred in certain cases, where a separate acid-purifying plant is not available, or when it is not necessary or desirable to use such a plant. If a sulphuric-acid-purifying plant is available, however, or if it is planned to incorporate such a plant in a new complex, dilution is suitably halted when reaching a given content of between 50 and 500 g/t, whereafter the mercury precipitate is separated from the solution. At room temperature this mercury range corresponds to a sulphuric-acid concentration lying within the range of 65-75%. Thus, only a minor quantity of mercury remains in the solution, this quantity often constituting an insignificant percentage of the original mercury content of the acid, and can readily be removed by means of other suitable methods, for example, by precipitation with thiosulphate. Experience has shown that the thiosulphate is best added to the solution subsequent to diluting the acid to at least concentrations in the range of 70-85%  $H_2SO_4$ . It is also possible, and particularly suitable to purify the sulphuric acid together with other sulphuric acid containing moderate quantities of mercury and having approximately the same concentration range as, for example, sulphuric acid obtained from pre-drying stages in a multi-stage system, as described in more detail hereinafter. As beforeindicated, it is naturally also possible to utilise dilution precipitation according to the invention while adding sulphur dioxide for the purpose of further purifying the acid.

The method according to the invention can be carried out in many different ways within the scope of the claims, the preferred method being selected, in each individual case, with respect to the apparatus available, and with respect to any previous purifying processes which may have been carried out for the purpose of eliminating mercury from the sulphuric acid. For example, the method according to the invention can be advantageously applied in combination with a single-stage sulphuric-acid washing process, for example, of the kind described in DE-B-2 132 231, and will then positively influence the mercury absorption in the washing step, and provide a purer mercury product. The method, however, can be applied to particular advantage

in multi-stage, gas-cleansing and sulphuric-acid purifying plants of the so-called double-dryer kind, for example, in such systems as those described in SE-B-7 307 048-4 and DE-A-2 243 577, it being possible to further improve these plants and render them more effective. This also enhances the possibilities of working-up material that is rich in mercury, for example, mercury-rich sludge, obtained from gas-cleansing systems, since the load on the acid-purifying section of said systems will be greatly reduced. This results in a lower consumption of precipitating reagents, such as thiosulphate, for example and less filtering problems, thereby avoiding bottle-necks in the purifying systems. It is also possible to reduce the filtering resources in relation to present levels. The mercury load on the acid-purifying stages will normally vary in response to variation in the mercury content of the raw materials. Other, similar problems can be effectively overcome and the aforesaid variations smoothed out when applying the invention.

The fact that it is necessary to dilute a concentrated sulphuric-acid solution when purifying the solution in accordance with the invention may seem to be a disadvantage, although in actual fact only small amounts of water are required to effect the necessary dilution. Figure 1 is a diagram illustrating the extent to which dilution is necessary in the case of a 98%-sulphuric acid as a function of the desired sulphuric-acid concentration in percent by weight. For example, the diagram shows that dilution from 98% to about 65%, which lies well beneath the upper limit for dilution according to the main claim, requires the addition of only 0.5 ton of water per ton of acid. It should be noted in this connection that the water is added to a part-flow of the concentrated acid, this part-flow corresponding approximately to only 0.5-2% of the total acid produced, and hence the total amount of water added is actually quite moderate.

A preferred embodiment of the method according to the invention will now be described in more detail with reference to Figure 2, in

which a so-called double-dryer system having a separate sulphuric-acid purifying plant is utilised for drying and cleansing roaster gases and for purifying the sulphuric acid produced.

5 A plant for producing sulphuric acid in accordance with the contact method comprises a pre-drying tower 1, and an after-drying tower 2, a contact apparatus 3, and an absorption tower 4. A moist roaster gas containing sulphur dioxide and also elementary mercury is supplied to the pre-drying tower 1, via a line 5. When the roaster  
10 gas obtained from the roasting process contains solid mercury compounds, these are effectively captured, for example, in the water wash, which takes place in a washing tower (not shown), preceding the drying apparatus, where the gas is saturated with water. The gas is dried in the pre-drying tower 1, with sulphuric acid, in a closed  
15 circuit, the sulphuric acid being supplied to the drying-tower 1, through lines 14 and 7. The sulphuric acid contacts the gas in the tower 1 in counter-flow, and the major part of the water contained by the gas is taken-up in the acid. This lowers the concentration of the acid. The concentration, however, should not be permitted to  
20 fall below 70-85%, since the vapour pressure above the acid would be much too high to obtain effective drying of the gas. About 10% of the elementary mercury accompanying the gas is absorbed in the acid in this circuit.

25 The gas is passed from the pre-drying tower 1, to the after-drying tower 2, through the line 41, and is passed from said after-drying tower through the line 42, to the contact apparatus 3, and from there through the line 43, to the absorption tower 4, and finally in the form of residual gases to the chimney, through line 44. The  
30 acid is passed from the pre-drying tower 1, through the line 8 to the separation tank 9, and from there to an acid cooler 11, by means of a circulation pump 10, where the acid is cooled indirectly with water to a temperature of 20-100°C, preferably 30-80°C, the water being supplied through line 12, and removed through line 13.  
35 Additional acid can be supplied to the tower 1, through line 6. This acid may comprise acid obtained from external sources or acid

recycled from the same plant. Subsequent to being cooled, the acid is returned to the pre-drying tower through line 14 and 7. Chilled acid is tapped-off through line 15, and passed to a mixing tank 16, where a thiosulphate solution is supplied to said acid through line 17, and optionally also water through line 18, in order to improve the precipitation of mercury.

The sulphuric acid is passed from the mixing tank 16, through line 19, to a separation means 20, where precipitated solid material containing the mercury content of the sulphuric acid is separated out. The separation means 20, may comprise a filter press, a centrifuge filter or some other suitable apparatus capable of separating out the solid precipitate. The material separated from the sulphuric acid in the separator 20, comprises sludge containing from 1% up to 10% mercury, and can be advantageously transferred to the roaster and there incinerated, since the invention enables a high mercury load to be placed on the acid system, and even presumes an accumulation of mercury in the acid in subsequent drying stages, where the major part of the elementary mercury present is taken-up.

The sulphuric acid is taken from the separator 20, and passed through line 21 to the circulation circuit 22, connected to the absorption tower 4. A small part of the sulphuric acid can also be removed in dilute form as product acid through line 47. If the amount of sulphuric acid passed through the circuit 22 is not sufficient to absorb the sulphur trioxide formed in the contact 3, water can be supplied to the circulation circuit through line 23. The sulphuric acid is passed through line 24, to the absorption tower 4, and from there to a circulation tank 26, and a circulation pump 27, through line 25. The acid in said circulation circuit is cooled indirectly in the cooler 28, by means of cooling water supplied through line 29, and is removed through line 30. The concentrated acid formed in the absorption tower 4 is removed as product acid through line 31. Concentrated sulphuric acid is passed to the

after-drying tower 2, through line 34, where the roaster gas is dried sufficiently for said gas to be passed to the contact 3. In addition, of the total amount of gaseous mercury accompanying the gas to the after-drying tower more than 95% will be absorbed in the sulphuric acid.

The sulphuric acid is passed from the after-drying tower 2 through line 35 to the circulation tank 36 and the circulation pump 37. If necessary, the acid is cooled indirectly in a cooler 38, water being supplied to said cooler through line 39 and removed through line 40.

In the second stage, there is maintained a strongly oxidizing environment, to facilitate the absorption and oxidation of mercury. In this stage, the sulphuric-acid concentration is held at 95-103% by introducing  $\text{SO}_3$  directly in separate towers, which are in circulatory connection with the washing tower, or directly to the second washing stage, through line 45, or by supplying oleum from a separate oleum-production tower (not shown). The advantages obtained with a high sulphuric-acid concentration in this stage are that a high oxidation potential is obtained and that only a small amount of sulphuric acid is produced in this stage. A bleed corresponding to the amount of acid produced in the circulation circuit 33, together with any acid supplied thereto, is taken from said circuit. In this connection, if found necessary or desirable, a minor part is taken through line 46, and supplied to the pre-dryer 1, through line 14. The major part of the bleed is passed through a line 48 to a diluting reactor 49, where the acid is diluted to a sulphuric-acid concentration beneath about 80% by adding water through line 50, whereupon a crystallised product rich in mercury sulphate is obtained. The acid is cooled by means of a coolant in a cooling element 51, in order to maintain a suitably low temperature. Alternatively, the acid can be diluted by supplying a part-flow of the moist sulphur-dioxide containing gas from line 5 to the vessel 49, through a line 5A. The dried gas is then passed

- through line 41A, back to the main-gas line 41 downstream of the pre-dryer 1. The diluted acid containing precipitated mercury products is then passed through a line 52, to a separating means 53, which may have the form of a simple sedimentation vessel, a filter, or some other conventional separating means, where the mercury sulphate and/or mercury is separated out and removed, as indicated by the arrow 54. The thus diluted acid, which now contains less mercury, is removed, as illustrated by the arrow 55, and passed through the pre-drying tower 1, through line 6, the remainder of the mercury present in the acid being precipitated out in the acid-purifying stages 16 and 20, whereupon a mercury precipitate can be removed from the system or recycled in the process, for example, back to the roaster. By recycling precipitate to the roaster, it is thus possible to recover more mercury in the form of a high-grade product, since this product can then constitute the sole mercury bleed in the process. The high-mercury content of the circulation circuit 33, can also be maintained by supplying mercury-containing sludge to said circuit.
- The effect which dilution and acid temperature has on the residual mercury-content of the acid is illustrated in Figures 3 and 4. Figure 3 is a diagram illustrating how a 98%-sulphuric acid having an original mercury content of about 2,000 g/t behaves when diluting to extremely low acid concentration at a temperature of about 20°C. Progressively more of the mercury content is precipitated as a product rich in mercury-sulphate by progressive dilution to approximately 65%. If the sulphuric acid is diluted still further, however, the precipitate will re-dissolve and when dilution reaches 20% substantially the whole of the mercury content is redissolved. The mercury content throughout the diagram corresponds to grams per ton of original undiluted acid. The diagram also illustrates by means of a broken line how the solubility increases at sulphuric-acid concentrations in excess of about 80%.
- When dilution is carried out while adding sulphur-dioxide to the solution, however, the separation of mercury can be continued even

when concentrations beneath 65% are obtained. In this case, when a sulphuric-acid concentration of about 40% is reached, mercury begins to precipitate in an elementary metallic form. Residual contents as low as less than 1 g/t can be obtained, which corresponds approximately to 0.15 g/t calculated on the diluted acid. This means that the final purification stage can also be carried out by means of dilution, when sulphur dioxide is added at the same time and when a final concentration of beneath 40% sulphuric acid can be accepted for process reasons.

Figure 4 illustrates the solubility of mercury in 62%-acid as a function of temperature, and thus also illustrates how the solubility curves of Figure 3 are dependent upon the acid temperature. Thus, a temperature higher than 20°C displaces the curves slightly upwards in Figure 3.

#### Example I

57000 m<sup>3</sup>/h roaster gas having an SO<sub>2</sub>-content of 12% and an Hg<sup>0</sup>-content of 1.75 mg/m<sup>3</sup> were passed through a plant according to Figure 2. Between 300 and 600 t/h sulphuric acid having a concentration of 80% and 98% respectively were circulated in each of the drying circuits. 16 tons of acid, containing 0.5 g/t mercury were removed each hour from the circuit containing 80% acid, for mercury precipitation, this acid being passed to the absorption circuit as purified 80% acid containing 0.5 g/t mercury subsequent to being purified in the sulphuric-acid purifying circuit (16,20) by precipitation with sodium thiosulphate.

0.2 tons of acid containing about 450 g/t mercury was bled-off each hour from the circuit containing the 98% acid, and passed to the



dilution stage, whereupon the mercury content was lowered by crystallisation and precipitation of mercury sulphate. When a sulphuric acid content of about 65% was reached, the mercury content had fallen to 100 g/t as a result of crystallization. By  
5 bleeding-off acid from the last drying stage and by diluting the separated mercury in accordance with the invention, approximately 60 g/h high-grade mercury is separated out, while only about 35 g/h mercury is separated out in the sulphur-purifying stage, in the form of a filtercake containing about 3% Hg. 30 tons of acid having a  
10 sulphuric acid content of 98.5% and a mercury content of only 0.18 grams were produced each hour in the said plant.

#### Example 2 a

15 A similar gas to that described in Example 1 was charged, in similar amounts, to a plant of the kind according to Example 1, but lacking a separate sulphuric-acid purifying circuit. 16 tons of acid having a mercury content of 0.64 grams were passed each hour from the 80%-acid circuit directly to the absorption circuit 22. The same  
20 amount of acid as that recited in Example 1 (0.2 t/h) was bled-off from the 98%-acid circuit, and diluted in the same manner as in Example 1, i.e. to an approximately 65%-acid and a mercury content of 100 g/t. 60 grams of high-grade mercury were removed each hour from the diluting reactor, while the diluted 65%-acid was passed  
25 to the absorption circuit. 32 tons of 98.5%-acid having a mercury content of 0.8 grams were removed hourly from said plant.

#### Example 2 b

30 The same method as that recited in Example 2a was carried out, with the exception that the acid was diluted to 37%, which is the lowest content which can be tolerated in said system at prevailing operating conditions. As a result of this further dilution with the addition of sulphur dioxide, it was possible to reduce the mercury  
35 content of the diluted acid to about 1 g/t. It was possible to produce

in the plant the same amount of acid as that in example 2a, but with a mercury content of only 0.4 g/t.

5 It will be seen from Examples 2a and 2b that the method according to the invention can very well be carried out in a double-dryer plant which also lacks a separate sulphuric-acid purifying stage, without the amount of mercury in the sulphuric-acid produced becoming prohibitively high, at least at normal input mercury contents. In many cases, a mercury-content of up to one gram per ton of  
10 acid can be fully acceptable.

### Example 3

15 57,000 m<sup>3</sup>/h roaster gas having an SO<sub>2</sub>-content of 12% and an Hg<sup>0</sup>-content of 7.2 mg/m<sup>3</sup> were charged to a plant according to Figure 2. From the drying circuit with 80%-acid, in which about 30 g/h mercury was taken-up from the gas, about 16 tons of acid were taken each hour for mercury precipitation, said gas containing 2.1  
20 g/t mercury, which acid subsequent to being purified in the sulphuric-acid purifying circuit by precipitation with sodium thiosulphate was passed to the absorption circuit as purified 80%-acid containing about 0.1 g/t mercury. The acid in the absorption circuit absorbs about 10 g/h mercury from the gas.

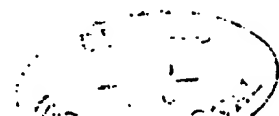
25 From the circuit containing a 98%-acid, in which about 370 g/h mercury was taken-up from the gas, there was bled-off 0.2 t/h acid containing about 1875 g/t mercury, and passed to the acid diluting stage, whereupon the mercury content fell, through crystallisation and precipitation of mercury-sulphate. Simultaneously with reaching  
30 a sulphuric-acid content of about 65%, the mercury content fell to 100 g/t. In this way, approximately 340 g/h of high-grade mercury was separated from the diluting stage, while only about 62 g/h mercury was separated out by precipitation with thiosulphate in the sulphuric acid purifying stage.

35

13 tons of acid having a mercury content corresponding to 3.5 grams were passed each hour from the absorption circuit to the pre-drying circuit.

- 5      30 tons of acid having a sulphuric acid content of 98.5% and a mercury content of only 0.27 grams were produced each hour in the plant.

10      Of these examples, Example 1 illustrates that a highly pure sulphuric acid can be produced from a gas having mercury contents which are normal for pyrite roasting processes and that only about 35% of the mercury charged to the system need be precipitated with precipitating agents in the sulphuric acid purifying stage, whilst 60% is precipitated during the dilution stage. Example 2 illustrates that  
15      in the case of a gas having a mercury content according to Example 1, it is possible to produce sufficiently purified sulphuric acid, without employing a separate mercury-precipitation process in the sulphuric-acid purifying stage. Thus, all mercury is bled off in the dilution stage. In this respect, Example 2a illustrates the result  
20      obtained with relatively moderate dilution, while Example 2b illustrates the maximum dilution which can be achieved without disturbing the liquid balance of the process. Example 3 illustrates the flexibility of the method, by applying said method to a roaster gas that is extremely rich in mercury and which is of the kind  
25      generated when roasting zinc concentrates rich in mercury. As will be seen, a highly pure product acid is obtained, despite the high mercury input.



CLAIMS

1. In the production of sulphuric acid from sulphur-dioxide containing gas, generated when treating raw materials and intermediate products containing mercury, a method for obtaining purer sulphuric-acid and for obtaining a high grade mercury product, in which method the gas is cleansed from accompanying gaseous mercury by bringing said gas into contact with a sulphuric-acid solution in one or more stages, so that the major part of the mercury is absorbed and dissolved in a concentrated solution having a sulphuric-acid concentration of at least about 85%, whereafter the purified gas is passed to a contact plant for the production of pure sulphuric acid, characterised by removing a part quantity of the concentrated sulphuric-acid solution and diluting said part quantity to a sulphuric-acid concentration of about 80% or there below, the major part of the mercury dissolved therein being precipitated therefrom as a high-grade mercury product which, if so desired, is separated from the solution; and in that the sulphuric-acid solution is then optionally purified of residual, dissolved mercury, whereafter the sulphuric-acid solution is removed for use in its present form, or is returned to an absorption tower in the contact apparatus for the production of pure, concentrated sulphuric acid.
2. A method according to claim 1, characterised in that the concentrated sulphuric-acid solution is diluted to a concentration exceeding about 50%, preferably exceeding 60%.
3. A method according to claim 1 or claim 2, characterised by diluting the sulphuric acid solution until a residual mercury content of 50-500 g/t is reached, and by then separating the high-grade mercury product from said solution and purifying said solution of residual dissolved mercury.
4. A method according to claim 3, characterised by separating residual mercury in the sulphuric-acid solution, by adding thereto

thiosulphate or some other agent capable of forming finely divided sulphur in said solution.

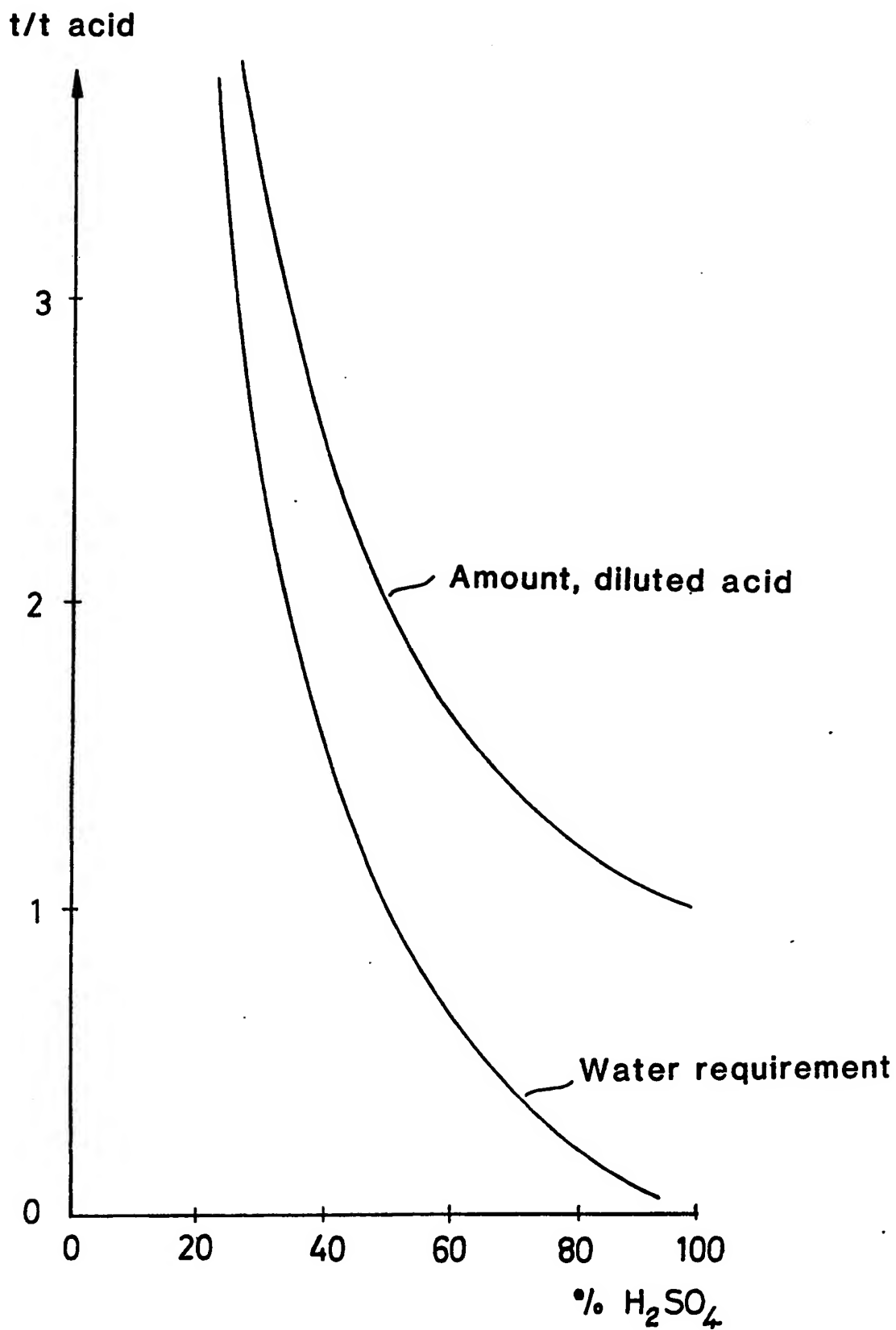
5        5. A method according to claim 3, characterised in that residual mercury in the sulphuric-acid solution is separated out by further diluting the acid in the presence of sulphur- dioxide.

10       6. A method according to claim 5, characterised in that residual mercury in the sulphuric acid solution is separated out by diluting the solution to a sulphuric-acid concentration beneath about 40%, while supplying sulphur dioxide to said solution, elementary mercury being recovered from said solution.

15       7. A method according to any one of claims 1 - 6, in which the gas is purified in a plurality of stages having gradually increasing sulphuric-acid concentrations, characterised in that the sulphuric-acid solution cleansed of the major part of said mercury and obtained from the last stage is passed to an earlier stage and purified from residual mercury together with the solution from said stage.

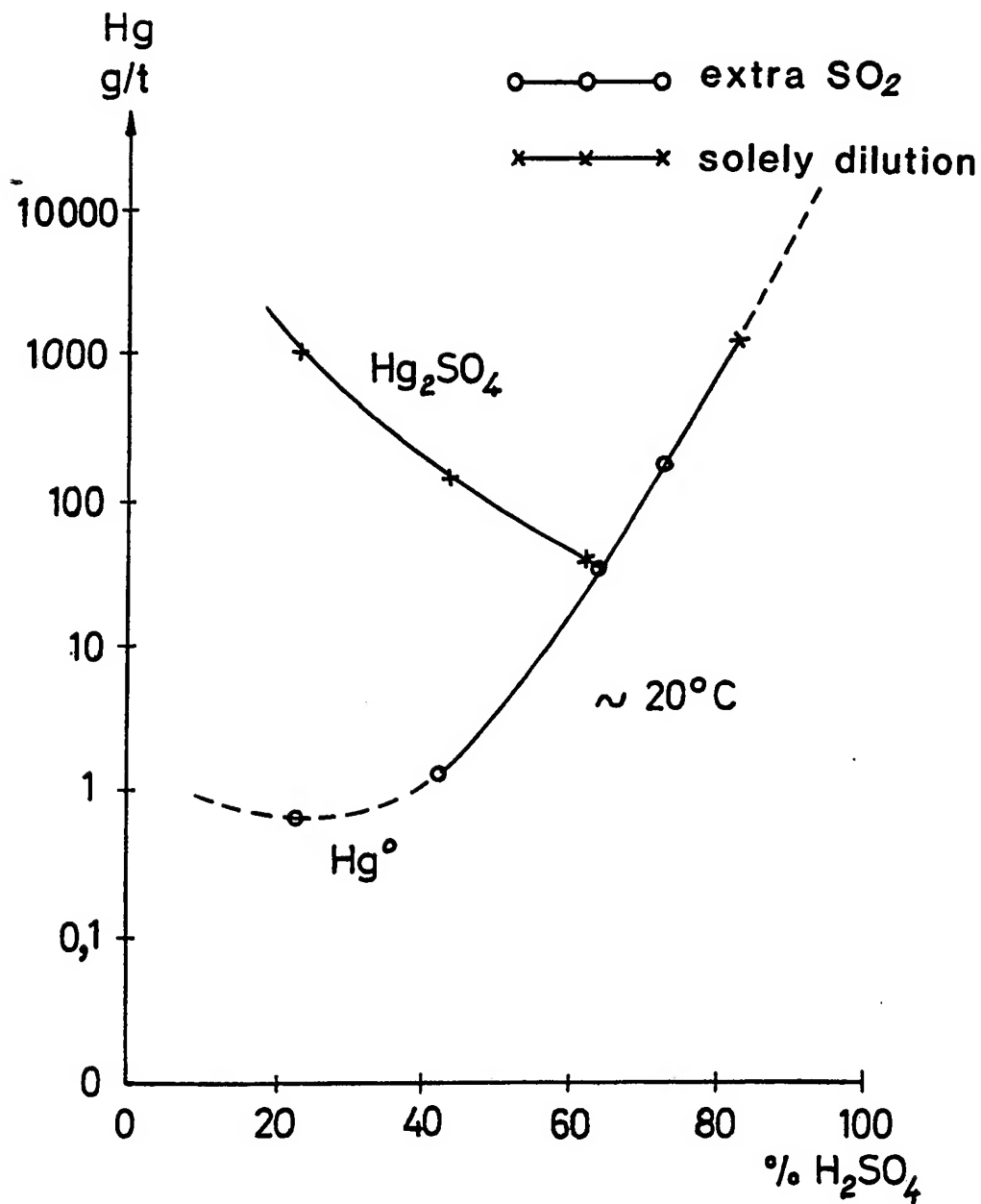
20       8. A method according to claim 1, characterised in that the sulphuric-acid solution in the presence of sulphur-dioxide is diluted to a residual mercury content of beneath 50 g/t preferably of beneath 10 g/t, wherafter the separated high-grade mercury product  
25       is removed from the solution, which solution is then supplied directly to an absorption tower in the contact apparatus.

30       9. A method according to any one of claims 1 - 8, characterised in that the high-grade mercury product is separated from said solution by sedimentation or filtration.

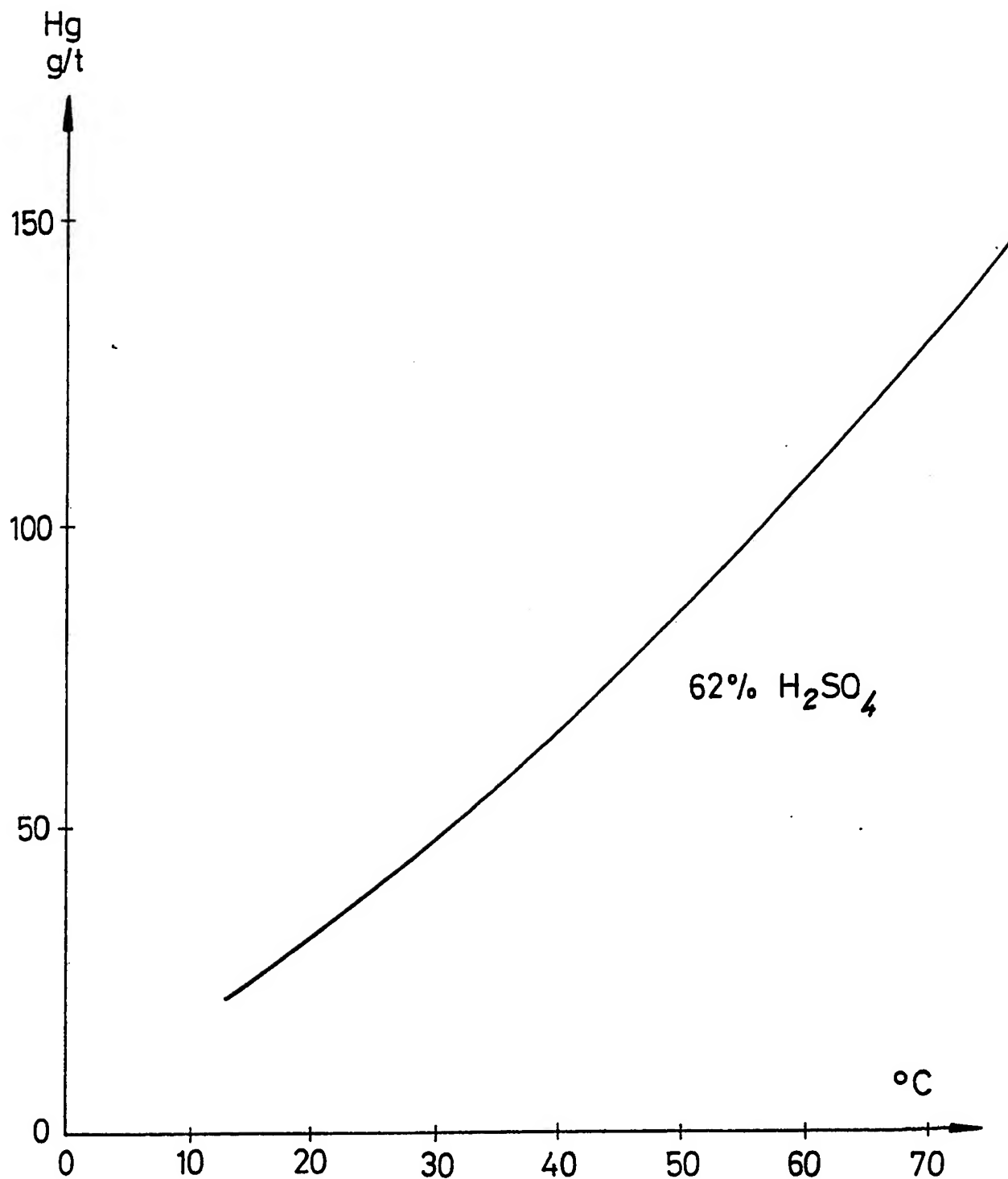


**Fig. 1**



**Fig. 3**



**Fig. 4**

# INTERNATIONAL SEARCH REPORT

International Application No PCT/SE83/00420

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC 3		
C 01 B 17/56, 17/74, 17/90		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC	C 01 B 17/56, 74, 765, 90; B 01 D 53/34	
US C1	423:531, 210; 55:72	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
SE, NO, DK, FI classes as above		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> 14		
Category *	Citation of Document, 15 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
A	DE, A, 2 132 231 (OUTOKUMPU OY) 17 February 1972	1
A	SE, B, 394 659 (MITSUI MINING & SMELTING CO) 4 July 1977	
X	SE, B, 396 361 (BOLIDEN AB) 19 September 1977 & NL, 7406693 FR, 2229642 BE, 815167 DE, 2423815 US, 3932149 AU, 69086/74 GB, 1438601 AU, 475870 CA, 1019134 JP, 50032094	
X	DE, A1, 3 213 685 (OUTOKUMPU OY) 18 November 1982 & GB, 2098186 JP, 57188407 AU, 82603/82	
<p>* Special categories of cited documents: 16</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (see specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search *	Date of Mailing of this International Search Report *	
1984-02-02	1984-02-24	
International Searching Authority *	Signature of Authorized Officer 20	
Swedish Patent Office	Britt-Marie Lundell	